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## The glass transition near the free surface

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### 1. Introduction

The influence of the intrinsic geometrical constrain such as the liquid/vapour interface on the glass transition phenomenon was investigated by several experimental techniques involving synchrotron radiation. The structure near the surface of the model organic glass former, dibutyl phthalate (DBP)  $C_{16}H_{22}O_4$ , was characterized by using grazing-incidence X-ray diffraction and X-ray reflectivity measurements. The dynamics at large length scales was examined with X-ray Photon Correlation Spectroscopy (XPCS). Relaxation data collected in the temperature range from RT down to 186K support the stretched relaxation scheme with stretching parameter  $\beta=0.85$ . Both, dynamic and static data were analyzed in the light of a Voigt-Kelvin model.

### 2. Experimental details and results

The experiment was performed at the beamline ID10A at the European Synchrotron Radiation Facility (ESRF) in France. Using 8keV radiation the surface sensitivity of the measurements was established by fixing the angle of incidence of the incoming X-ray beam at 0.12 degree, which corresponds to around 80% of the critical angle  $\alpha_c$  of total external reflection.

The cryostat, an improved version of the liquid sample cell described in [1] was used to control the temperature of the high purity dibutyl phthalate DBP (CAS: 84-74-2) with an accuracy around  $\pm 20$ mK over a period of more than 24h. The sample was injected into a 0.3mm deep (120mm in diameter) trough and encapsulated inside the inner Cu chamber. The temperature of the liquid was controlled by adjusting the flow of the liquid nitrogen through the base part of the inner chamber. The large area of the trough minimizes the influence of the meniscus on the distribution of the reflected intensity. Both, the inner chamber and the volume between the inner and the outer chamber were evacuated to around  $10^{-1}$ mbar and  $10^{-4}$ mbar, respectively. The temperature of the sample was tuned from 260K to 186K with an average cooling rate  $\sim 0.3$ K/min. In order to stabilize the sample environment, at each temperature point setup was kept for 1h at given conditions before starting the measurements.

In XPCS experiment, the dynamics of the sample is described by means of the normalized intensity autocorrelation functions, defined as [2]

$$g_2(\tau) = \langle I(t+\tau)I(t) \rangle_t / \langle I(t) \rangle_t^2$$

where  $I(t)$  is the intensity at time  $t$ .

The aim of the measurements was to determine the  $q$ -dependence of  $g_2(\tau)$  as the temperature of the samples approaches the glass transition  $T_g$ . Starting from 260K, the

shape of  $g_2(\tau)$  indicated the existence of only the pure overdamped capillary waves at the surface of DBP. Furthermore, the decay of  $g_2(\tau)$  can be modelled only when the stretched exponential decay scheme is assumed. In this case, the shape of  $g_2(\tau)$  can be described by the following formula

$$g_2(\tau) = 1 + g_0 \exp(-2\tau / \tau_0)^\beta$$

where  $g_0$  is a contrast, describing the degree of coherence,  $\tau_0$  is characteristic time constant, and  $\beta$  is a stretching parameter, which for our data sets was found to be equal to 0.85. Typical  $g_2(\tau)$  curves are shown in fig. 1.

Fig.2 summarizes the relaxation times measured for different values of  $q$  at different temperatures. The striking feature of all  $\tau_0$  vs  $q$  curves is that their shape can not be explained using the capillary waves CW approach. To model the data the viscoelasticity of DBP must be taken into account. The Voigt-Kelvin model predicts  $\tau_0$  vs  $q$  to have following form [3]

$$\tau(q_{||}) = \left( \frac{2q^2 \eta}{\omega_s^2 \rho} \right) / \left( 1 + \frac{2q^2 \mu}{\omega_s^2 \rho} \right)$$

where  $\omega_s = \sqrt{\frac{\gamma}{\rho}} q^3$ ,  $\gamma$  is the surface tension,  $\rho$  is the density,  $\eta$  denotes viscosity, and  $\mu$  is the frequency independent shear modulus. The gravity effect has been neglected in the data analysis.

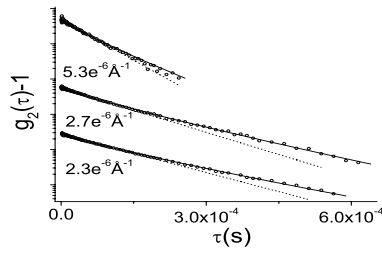


Fig. 1 The  $g_2(\tau)$  functions collected at 260K together with corresponding calculated curves for  $\beta=0.85$ (solid), and  $\beta=1$ (dotted) .

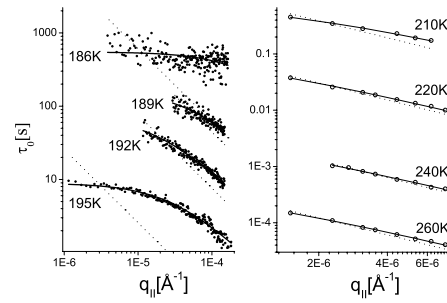


Fig. 2 The  $\tau_0$  vs  $q_{||}$  data sets collected at different temperatures fitted with capillary waves model (dotted line) and viscoelastic model (solid line).

### **3. Conclusion**

In summary, we report time correlation spectroscopy results of supercooled dibutyl phthalate. The sample clearly shows viscoelastic properties in a broad temperature range. Also the stretched exponential scheme has been observed to govern the relaxation of DBP.

### **References**

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